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FERROCENE

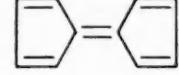
By JACQUE K. LINDSAY*

Introduction

To the rapidly expanding field of organometallic chemistry has been added a new and significant class of compounds described by the American investigators as having a "sandwich structure" (1) and by the German authors as a "Doppelkegelstruktur" (2). The discovery and preparation of bisdicyclopentadienyliron in 1951 by Kealy and Pauson (3) provided the parent compound (I) in this novel organometallic class.



I



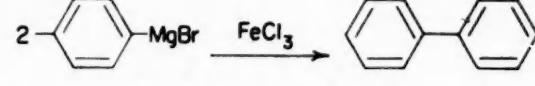
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Historical

While seeking a route to fulvalene (II) by the oxidation of cyclopentadienylmagnesium bromide with anhydrous ferric chloride, in the manner in which biphenyl is prepared from phenylmagnesium bromide, a strange orange crystalline compound

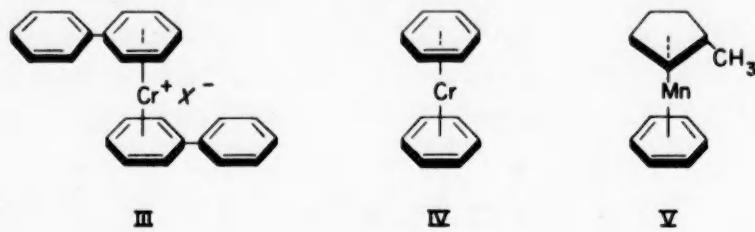


was obtained instead of the expected dihydrofulvalene. The compound analyzed for $C_{10}H_{10}Fe$ was soluble in most organic solvents and displayed unusual stability towards acids and bases. Independently, and at about the same time, Miller, Tebboth, and Tremaine (4) prepared the same compound by heating powdered iron with cyclopentadiene at $300^{\circ}C$. in a nitrogen atmosphere. It was soon recognized that this compound displayed properties of an aromatic system, and the name "ferrocene" was proposed (5) which is now the commonly accepted name for bisdicyclopentadienyliron.

Since the discovery of ferrocene in 1951, more than forty cyclopentadienyl and related structures, involving transition and rare-earth metals, have been reported

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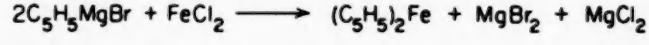
in well over one hundred technical publications. As early as 1921, Hein (6) reported unusual chromium salts, among them III, the structure of which was described in 1957 by Fischer and Seus in connection with their work on dibenzenechromium (IV) (7). Recently, the first mixed "sandwich" compound (V) was reported by Coffield,



Sandel, and Closson (8). While it is not the purpose of this article to review this entire area of research, these examples may serve to illustrate the vastness of this new field of chemistry. Excellent reviews on ferrocene have been prepared by Pauson (9) and Fischer (10) for those desiring more detailed information.

Preparation

While the original preparation of ferrocene involved the use of ferric chloride, the product appears to arise from a partial reduction of the ferric salt by the Grignard reagent; this may be represented best as a reaction involving ferrous chloride. Recently, a method of preparation using ferrous chloride was reported to



give ferrocene in excellent yields (11). Ferrocene is also produced in good to near-quantitative yield by the action of anhydrous ferrous chloride on the sodio derivative of cyclopentadiene in liquid ammonia (12) or such solvents as tetrahydrofuran and 1,2-dimethoxyethane (11, 13). The method using tetrahydrofuran as a solvent affords one of the best laboratory procedures for the preparation of ferrocene and is described in "Organic Syntheses" (14). Other methods of preparation involve ferrous complexes (15) and the iron carbonyls (16).

Structure and Properties

Ferrocene (I) appears as an orange crystalline solid having a distinct camphor-like odor. The solid melts at 173°-174° C. without decomposition (3, 4) and is stable in the vapor phase up to 400° C. It is not attacked by water, boiling concentrated hydrochloric acid, or 10% sodium hydroxide solution (3). The material is slightly soluble in common organic solvents, such as ethanol, ether, benzene, and the petroleum ethers.

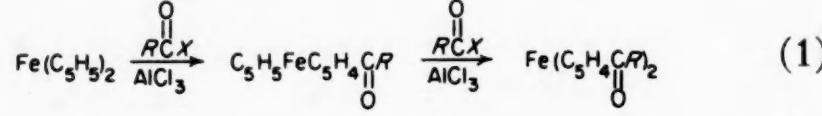
The essential feature of the molecule is what appears to be a single covalent bond linking the metal atom to the plane of each cyclopentadienyl ring. The exact nature of this nonclassical type of bonding is still not completely understood. Molecular orbital treatments of this problem have been published by Dunitz and Orgel (17) and Moffitt (18) which present the most reasonable bonding theories. The central iron atom is in a zero-valency state and each cyclopentadienyl ring contains the equivalent of two double bonds which are not usually shown in the structural formula, as contrasted with structures containing the benzene ring (III and IV). Each position on the cyclopentadienyl rings is equivalent.

Extensive physical measurements have been made on the molecule in the solid state and in solution. The dipole moment of ferrocene is essentially zero and the

molecule is diamagnetic. A molecular weight of 186 has been calculated, together with a normal boiling point of 249° C. The iron-to-carbon bond plus the resonance energy can be calculated as 113 kcal. (19), which is in agreement with the unusual stability of the compound. The mean iron-carbon distance is approximately 2.04 Å and the carbon-carbon distance near 1.40 Å. (9). The ultraviolet spectrum shows maxima at 325 m μ and 404 m μ and the infrared spectrum is strikingly simple. Two infrared peaks at 9.95 μ and 9.00 μ have proved useful in structural determinations. The peaks are retained in all monosubstituted ferrocene derivatives but disappear if both rings are substituted (20, 21).

Aromatic Character and Reactions

The reactions that the ferrocene molecule undergoes are mainly concerned with the "aromatic" nature of the cyclopentadienyl rings first demonstrated by Woodward, Rosenblum, and Whiting (5). These authors showed that ferrocene does not undergo addition reactions either with maleic anhydride or hydrogen in the presence of Adams's platinum oxide catalyst. The molecule was also found to undergo typical Friedel-Crafts acylations to yield either the mono- or diacetylated product (Equation (1)).



The more simple aromatic substitution reactions of ferrocene are not observed. Thus, nitration, halogenation, and sulfonation, under the usual conditions, lead to destruction of the molecule, presumably through the easily oxidized central iron atom. However, the sulfo- (22) and halo-derivatives have been prepared by more indirect methods (23).

Ferrocene is metalated with *n*-butyllithium to produce mono- and bislithioferrocenes (24, 25), which have been further carbonated to the carboxylic acids. The products proved identical with those obtained by oxidation of acetylferrocenes with sodium hypohalite (5, 21). These plus numerous other electrophilic and nucleophilic substitution reactions support the aromatic nature of ferrocene (26).

A second type of reaction involves the iron atom in the ferrocene molecule. This central atom is readily oxidized by a number of reagents to a singly charged, water-soluble, paramagnetic cation called the "ferricinium" ion (5, 15). The reaction is reversible and the cation may be reduced to the neutral molecule. The ferrocene-ferricinium system has an oxidation-reduction potential close to that of the ferrocyanide-ferricyanide system (9, 22, 27).

Applications

Only minor efforts have been directed to the commercialization of ferrocene and ferrocene-type compounds. Ferrocene has already demonstrated significant anti-knock properties in fuels (28). A related compound, methylcyclopentadienylmanganese-tricarbonyl, has proved twice as effective as tetraethyl lead (TEL) as an anti-knock agent, and, when used in conjunction with TEL, surprising synergistic effects are produced (29).

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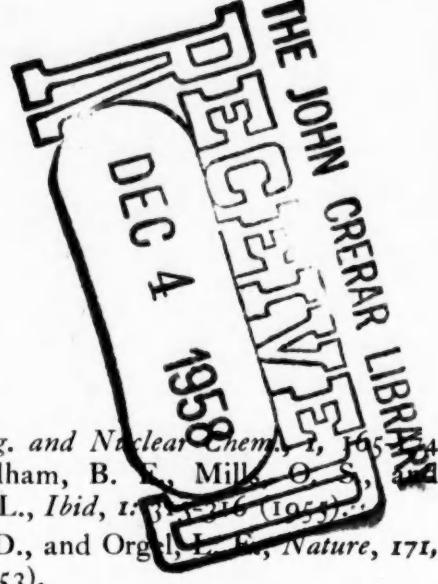
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